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SYNTHESIS OF POLYPHOSPHATE GLASSES

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Multicomponent spatially cross-linked polymers based on ultraphosphates with vitrification temperature 123 – 302°C have been synthesized. Their hydraulic stability (rate of mass loss when boiled in water) was measured and equals 0.0075 – 0.123 g/min. It is shown that there is a correlation between the vitrification temperature of polymers and their water resistance. A quantitative relation was obtained for the flow temperature and the vitrification temperature of the polymers: $t_f = t_v + (25 – 35)$°C. It is shown that in principle it is possible to obtain on the basis of ultraphosphates high-temperature inorganic thermoplastics with flow temperature varying over wide limits.

Key words: ultraphosphates, oxyfluoridated polymers, vitrification temperature, water resistance, flow temperature, inorganic thermoplastics.

Spatially cross-linked inorganic polyoxides, which belong to a class of common polymers, possess two fundamental advantages over organic polymers: exceptional thermal stability and inability to oxidize and burn [1 – 5].

At the same time inorganic polymers of this nature also possess extremely high flow temperatures; this greatly impedes the technology for forming materials based on them. In addition, the plasticity and impact viscosity of these polymers are low.

It is obvious that giving inorganic polymers low flow temperatures, close to the flow temperatures of organic polymers, while preserving their thermal tolerance would make it possible to decrease the process temperature substantially and thereby obtain a structural plastic with high heat tolerance. In addition, at such flow temperatures it becomes realistic to develop composite mixtures of inorganic and organic polymers, making possible to develop new structural materials.

The high flow temperatures t_f of inorganic polyoxides (SiO_2, TiO_2, Al_2O_3, silicate glasses) are due to two factors: the high density of the cross-linkage of a three-dimensional network and strong intermolecular interactions of the polarized chemical bonds of chains, the bonds being largely ionic.

However, the wide class of inorganic polyoxides contains polymers which possess anomalously low flow temperatures and make it possible to vary their relaxation properties widely, such as the ultra- and polyphosphates, whose vitrification temperature t_v can vary over wide intervals [6, 7].

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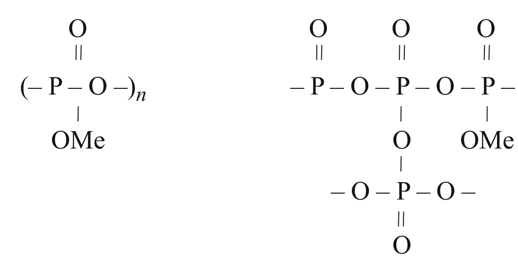
The chemical structure of linear and branched fragments of the polymer framework is as follows:



where Me is a univalent alkali metal (Li, K, Na).

There is another feature of polyphosphates which like all low-melting inorganic polyoxides possess low water stability — tendency toward hydrolytic splitting — and they are hygroscopic, which makes working with them practically impossible.

Thus there arises the problem of synthesizing polymers with acceptable vitrification temperatures but at the same time possessing adequate water resistance.

Therefore, before a wide search is undertaken the chemical composition of the polymer framework, whose modification could lead to the desired results, must be validated.

The dependence of the vitrification temperature polyphosphate glasses with the simplest structure on their chemical structure [7] shows that by varying the ratio of P_2O_5 and Me_2O it is possible to obtain polymers with very low values of t_v. In so doing it was concluded paradoxically that an increase in the number of cross-links is accompanied by a decrease of the vitrification temperature, explained by the fact

that the force of interaction of the fragments $\begin{array}{c} | \\ O \\ \| \\ -P-OMe^{+} \\ | \end{array}$ is larger than the rotation barrier of $\begin{array}{c} O \\ \| \\ -P-O \end{array}$. In addition, it was shown that t_v depends on the nature of the alkali metal and decreases with increasing ionic radius of the metal ion. Thus using potassium instead of sodium decreases the vitrification temperature of the polymer by ~ 60°C.

The data presented were experimentally confirmed during the synthesis of polyphosphates with different composition during the introduction of sodium and potassium cations (Fig. 1).

Thus, P_2O_5 and K_2O in the ratio 1 : 0.3 ~ 0.5 can serve as the main components of low-temperature phosphates, giving the minimum values of t_v.

There exist a number of devices for increasing the chemical stability and decreasing their vitrification temperature.

Double-Alkali Effect

The crux of the method consists in using as the constituent components of the polymer two univalent alkali metals simultaneously. The water resistance of the polymer is proportional to the difference of the ionic radii of the atoms and therefore it is better to combine the sources of the sodium and lithium atoms in the synthesis.

It has been shown that the effect is sharper in the range of total concentration of the metal oxides 10 – 17% [8]. In some cases, specifically, borophosphate polymers, it has been shown that t_v of the polymer decreases while its water resistance is preserved.

Boron Effect

Boron oxide can be use to increase the chemical stability of ultraphosphates. It has been shown that when B_2O_3 is introduced into ultraphosphates in the amount 5% (molar content) the water resistance of the polymer increases 20-fold; this is explained by the depolymerization of phosphate chains and the appearance of – B – O – P – [8, 9]. The appearance of bridge bonds – B – O – P – is most fully manifested for the ratios $Na_2O/B_2O_3 > 1/3$.

Fluoride effect

One method of lowering the vitrification temperature of polyphosphates is to introduce into the structure of the network a fluorine atom which breaks the polymer chain [10, 11]. The chain is broken with formation of a terminal group PO_3F. Replacement of oxygen by a fluorine atom decreases the average length of the chain and is accompanied by an increase of the intermolecular interactions and an increase of the packing density of the structure. Nonetheless the breaking of the polymer chain affects most the vitrification temperature and as a result decreases it.

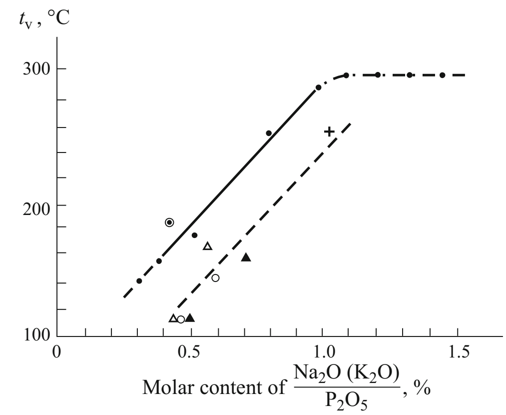


Fig. 1. Vitrification temperature of polyphosphates versus the ratio of P_2O_5 and Na_2O (K_2O): ●) sodium polyphosphates (13); ⦿) sodium polyphosphates (data of present authors); ▲) potassium polyphosphates (14); △) potassium polyphosphates (7); ○) potassium polyphosphates (data of present authors); +) melting temperature of K_2HPO_4.

Effect of Alkali-Earth Metals

It has been shown for many examples that introducing into polyphosphates alkali-earth metals MgO, BaO, CaO, as well as ZnO even in large concentrations makes is possible to obtain low-melting ultraphosphates [6, 7, 12]. The chemical stability of the glasses increases in the process.

The introduction of bivalent metals into a phosphate network of cations not only cross-links the polymer chains but also decreases the fraction of the acceptor-bonds of the protons $\begin{array}{c} O \\ \| \\ -P-O \end{array}$ as a result of the redistribution of the multiple bonds in the PO_4 tetrahehdron [13].

Our polymers were synthesized in water solutions. For this, the solutions, for example, phosphoric acid, boric acid, and salts of metals, are evaporated in the process of mixing to a reduction of the volume of the solution to 1/3 of the initial value. Next the solution was placed in a furnace and heated at 850 – 900°C for 0.4 – 2 h. The synthesized polymer was cooled in two regimes: natural cooling at room temperature and slow cooling in a furnace to 650°C followed by rapid cooling at room temperature. The latter regime was chosen on the basis of the data obtained in [14], where it is shown that for a slow decrease of the cooling temperature t_v of polyphosphates decreases.

On account of the strong volatility of fluorine the fluoridated polymers were synthesized in a stepped regime: $t = 200$°C — 1 h; $t = 300$°C — 1 h, $t = 450$°C — 1 h; $t = 850$° — 0.4 h. Cooling was done according to the second regime.

The glasses were synthesized in graphite and corundum crucibles. The DTA method was used to determine the heat tolerance of the polymers. The vitrification temperature of the polymers was measured by scanning calorimetry and the flow temperature by a thermomechanical method. The water

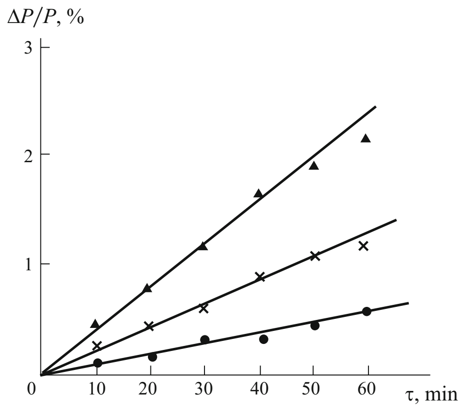


Fig. 2. Typical curves of the mass losses of ultraphosphates with holding in water ($t = 100°C$).

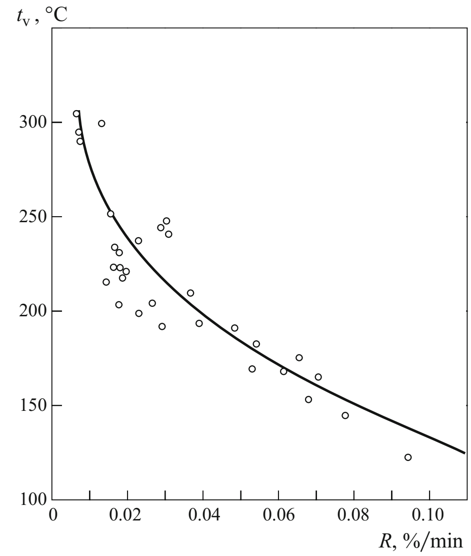


Fig. 3. Correlation between the vitrification temperature of ultraphosphates t_v and their mass losses R in water ($t = 100°C$).

resistance of the synthesized polyphosphates was determined from the mass loss of a 1 × 1 × 1 cm sample boiled in water.

The search for the optimal compositions of the polyphosphates and their synthesis conditions was conducted on the basis of the basic composition (molar content, %): P_2O_5 — 70 and Me_2O — 30 (see Table 1).

The optimal compositions of the polymers were obtained on the basis of the experimental data and the synthesis conditions of the polymers were studied.

Since one of the main parameters required to evaluate the properties of the polymers is their hydrolytic stability, the rates of dissolution of ultraphosphate polymers in boiling water were measured (Fig. 2) and an attempt was made to relate the vitrification temperature of the polymers and the water resistance R (Fig. 3). The correlation obtained can be stated by the plastification of the polymers by a water solution of the initial mixture and the measured value of t_v does not reflect the relaxation properties of the polymers themselves, which is confirmed by the mass losses of the polymers on heating > 600°C.

It is well known that the thermal stability of the ultraphosphates themselves is extremely high (synthesis occurs are $t = 850°C$) and thermal destruction can occur at much higher temperatures. For this reason it should be assumed that the measured mass loss of a polymer and the relation of this loss with the vitrification temperature reflect not the thermal stability of a chain but rather the energy of interaction of the water solution of the initial mixture with the polymer framework (Fig. 4).

Nonetheless, the values obtained for the temperature of the onset of the mass loss t_{ml} are very high compared with the values of this parameter which are characteristic even for high-temperature organic and organoelemental polymers.

The experience gained also shows that driving t_{ml} to 1000°C and higher without substantially increasing their vitrification point is a real problem.

The available results show that plastification and elastification of phosphate polymers by organic and organoelemental polymers are possible, which opens wide possibilities for developing composite materials for construction.

As one technique for lowering the vitrification temperature of ultraphosphates, the possibility of obtaining oxyfluoride polymers was examined. Fluorides were used for this purpose (see Table 1).

Taking account of the high volatility of fluorine, which impedes polymer synthesis, a wide interval of concentrations of its carriers was tested.

TABLE 1. Compositions of Ultraphosphates

Molar content, %												
P_2O_5	Li_2O	K_2O	Na_2O	B_2O_3	MgO	ZnO	BaO	Al_2O_3	HF	LiF	NaF	MgF_2
Experimental compositions												
56 – 83	2 – 10	30 – 35	4 – 30	4 – 5	2 – 25	2.5 – 30	2 – 5	25	5 – 20	2 – 5	5 – 20	4 – 16
Optimal compositions												
70	10	–	10	5	5	–	–	–	–	–	–	–
70	10	–	10	5	–	5	–	–	–	–	–	–
70	10	–	10	5	–	–	5	–	–	–	–	–

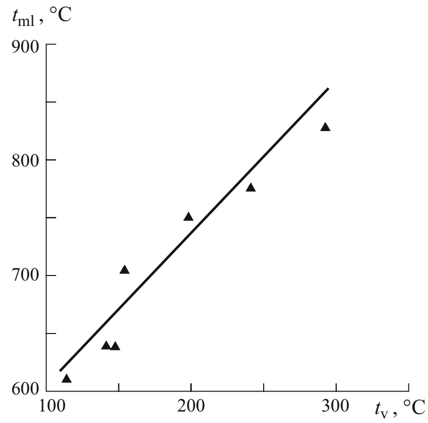


Fig. 4. Temperature t_{ml} of the onset of mass loss of ultraphosphates (DTA method) versus their vitrification temperature t_v.

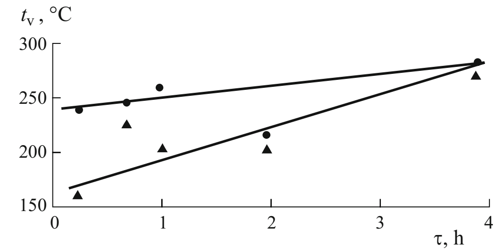


Fig. 5. Vitrification temperature of oxide (●) and oxyfluoride (▲) ultraphophates versus their synthesis time.

The results obtained indicate a quite appreciable decrease of t_v (Fig. 5). However, considerable experimental difficulties accompanying such synthesis resulted in the elimination of fluorides from the optimal compositions of the synthesized polymers.

Another important parameter characterizing the operational properties of construction materials is there inflammability.

In formulating the problem and choosing an experimental object, we examined a priori the possibility of using inorganic polyoxide, which is fundamentally inflammable, i.e. it does not oxidize rapidly in air.

It can be concluded on the basis of the studies performed that the path chosen for obtaining thermally highly tolerant polymers for developing construction materials at relatively low processing temperatures is promising.

Thus, multicomponent polymer ultraphosphates have been synthesized.

The methods of regulating the vitrification temperature of polyphosphates have been studied and it has been shown that polymers with vitrification temperature 123 – 950°C can be synthesized.

The flow temperature of the synthesized polyphosphates was measured and it was shown that

$$t_f = t_v + (25 - 35)°C.$$

A correlation was obtained between the vitrification temperature of polymers, their hydrolytic stability, and the inset temperature of the mass loss on heating.

It was shown that thermally highly tolerant inorganic thermoplastics with flow temperature varying over wide limits (for example, equal to the flow temperature of organic polymers), which opens up the possibility of combined processing of organic and inorganic polymers for the purpose of developing a new class of composite materials.

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